

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



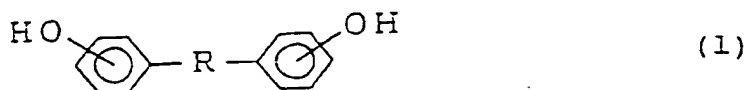
(11) Publication number:

0 648 415 A2

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **94307047.4**(51) Int. Cl.⁶: **A01N 31/08, A01N 43/80, A01N 25/22, //(A01N31/08, 43:80,25:22)**(22) Date of filing: **27.09.94**(30) Priority: **01.10.93 JP 246888/93**(43) Date of publication of application:
19.04.95 Bulletin 95/16(84) Designated Contracting States:
DE GB NL(71) Applicant: **KURITA WATER INDUSTRIES LTD.**
4-7, Nishishinjuku 3-chome
Shinjuku-ku
Tokyo (JP)(72) Inventor: **Yagi, Minoru, Kurita Water Ind.Ltd.**
4-7 Nishishinjuku 3-chome
Shinjuku-ku,**Tokyo (JP)****Inventor: Nakane, Kazumi, Kurita Water**
Ind.Ltd.**4-7 Nishishinjuku 3-chome**
Shinjuku-ku,**Tokyo (JP)****Inventor: Hiyane, Yuriko, Kurita Water Ind.Ltd.****4-7 Nishishinjuku 3-chome**
Shinjuku-ku,**Tokyo (JP)**(74) Representative: **Pendlebury, Anthony et al**
PAGE, WHITE & FARRER
54 Doughty Street
London WC1N 2LS (GB)(54) **Clathrate compound including water-soluble microbicide.**

(57) 1. A clathrate compound composed of a water-soluble microbicide and a phenolic compound of general formula (1):



wherein R represents an alkylidene group having from 2 to 4 carbon atoms,
or of general formula (2):



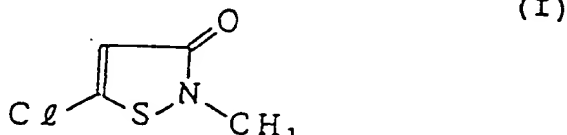
wherein R¹ and R² each independently represents an alkyl group having from 2 to 4 carbon atoms.

FIELD OF THE INVENTION AND RELATED ART STATEMENT

The present invention relates to a clathrate compound and, more particularly, to a novel clathrate compound including a water-soluble microbicide, which improves the handleability and the stability of the microbicide therein.

In water systems such as cooling water systems in various factory plants or the pulp and paper industries, slime of various bacteria, fungi, animals and vegetables adheres to the ducts or lines to cause various troubles.

Hitherto, for the purpose of preventing the troubles to be caused by slime or the like in such systems, a microbicide (slime-controlling agent) has generally been employed as it may easily be handled and it is relatively low-priced. For instance, 5-chloro-2-methyl-4-isothiazolin-3-one of the following formula (I) (hereinafter referred to as "CI-MIT") is widely used as a slime-controlling agent, a bactericide, an algicide or a fungicide for various water systems such as a cooling water system, a papermaking process system or a swimming pool, as it has an excellent microbicidal activity.



However, CI-MIT is extremely stimulative to the skin and a careful caution is necessary for handling the same, though it has an excellent microbicidal activity.

Since CI-MIT decomposes extremely easily, water-soluble microbicides on the market contain a large amount of Mg salts so as to stabilize CI-MIT therein. Therefore, such commercial microbicides could not be employed in the field of latex and emulsion which can not accept Mg salts.

The CI-MIT can be separated from the water-soluble microbicides on the market by extraction methods using organic solvents, but the thus-extracted CI-MIT is unstable especially under heat, so that it decomposes within one or two days even at about of 40 °C. For these reasons, special attention is needed to store the compound such as storing it in a refrigerator.

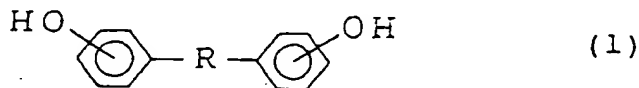
In order to overcome problems such as above, the present applicant has already proposed clathrate compounds having a water-soluble microbicide such as CI-MIT containing a host compound such as a bisphenol halide (Japanese Patent Laid-Open Application No. 1-190602).

Among the host compounds proposed in Japanese Patent Laid-Open Application No. 1-190602, 2,2'-methylenebis(4-chlorophenol) has been considered preferred.

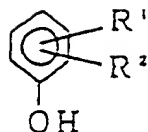
OBJECT AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved clathrate compound including a water-soluble microbicide such as CI-MIT.

The clathrate compound of the present invention is, characterized by comprising a water-soluble microbicide and a phenolic compound of the following general formula (I) or (2):



wherein R represents an alkylidene group having from 2 to 4 carbon atoms.



(2)

wherein R¹ and R² each represent an alkyl group having from 2 to 4 carbon atoms.

As the water-soluble microbicide, preferred is CI-MIT having the above-mentioned structural formula (I).

Specifically, the clathrate compound of the present invention is composed of a water-soluble microbicide such as CI-MIT, as the guest compound, and the above-mentioned phenolic compound, as the host compound, in such a way that the host compound includes the guest compound therein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Bisphenolic compounds of formula (I) to be used in the present invention include, for example, 4,4'-ethylidenebisphenol, 2,4'-isopropylidenebisphenol, 2,2'-vinylidenebisphenol, 4,4'-isobutylidenebisphenol, 2,6'-sec-butylidenebisphenol, etc.

Phenolic compounds of formula (2) also to be used in the present invention include, for example, 2,4-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,4-di-propylphenol, 2-propyl-4-tert-butylphenol, etc.

The water-soluble microbicide for use in the present invention may be any one that may form a clathrate compound with the above-mentioned phenolic compound. CI-MIT which is widely used as an effective microbicide is preferable, but this is not limitative.

The clathrate compound of the present invention, comprising such a water-soluble microbicide and a phenolic compound, may easily be prepared by reacting them in an organic solvent or in water.

When an organic solvent is used for preparing it, a solution prepared by dissolving any of the above-mentioned phenolic compounds in an ordinary organic solvent such as methanol, ethanol or acetone is mixed to a water-soluble microbicide such as CI-MIT or with a mixture containing a water-soluble microbicide such as CI-MIT and some impurities, etc., and reacted with a water-soluble microbicide. Accordingly, the intended clathrate compound precipitates out as a solid product, which is filtered and separated by ordinary methods.

When water is used for the same, the above-mentioned phenolic compound is directly added to an aqueous solution containing a water-soluble microbicide to be the guest compound, and mixed by stirring. The aqueous solution to be used is not limited to one containing only a water-soluble microbicide to be the guest compound. As like as the above-mentioned case using an organic solvent, the solution may contain some impurities. The above-mentioned phenolic compound reacts with a water-soluble microbicide with high selectivity. Therefore, even when a water-soluble microbicide containing impurities such as side products may be used directly as the raw material, a desired clathrate compound including selectively only the intended water-soluble microbicide may be obtained.

The reaction temperature may range from 0 °C to 100 °C. In general, it is approximately from 10 °C to 30 °C. The reaction time is about from 0.5 to 24 hours.

After the reaction, the clathrate compound is generally obtained as a solid product, which may be separated from the aqueous phase, washed with water and dried. Thus, the intended clathrate compound of the present invention is obtained.

The molar ratio between the water-soluble microbicide such as CI-MIT and the above-mentioned phenolic compound of formula (I) both constituting the clathrate compound of the present invention, is generally such that (water-soluble microbicide):(phenolic compound (1)) is from 1:0.2 to 1: 5. The molar ratio between the water-soluble microbicide such as CI-MIT and the above-mentioned phenolic compound of formula (2), both constituting the clathrate compound of the present invention, is generally such that (water-soluble microbicide):(phenolic compound(2)) is from 1:0.2 to 1: 5.

The clathrate compound of the present invention, thus obtained in the manner mentioned above, is generally powdery and may easily be shaped into tablets. Since the water-soluble microbicide is included as the host compound, the clathrate compound is low in toxicity and is easy in handling thereof, and the microbicide is prevented from reacting with other substance to lower its microbicidal activity during its use.

When the clathrate compound of the present invention is put into water, the host water-soluble microbicide in the clathrate compound is delayed to release therefrom. For example, when a clathrate compound of the present invention including 3 % by weight of CI-MIT therein is put into water, the amount of CI-MIT to be released from the clathrate compound into water is as low as several 100 mg/liter. Therefore,

a water-dispersible preparation containing a clathrate compound of the invention having the above-mentioned CI-MIT concentration (3 % by weight) is extremely preferred, as its stimulation to the skin is much lowered. The compound of the present invention may be applied to a slow-release microbicide which slowly releases its active ingredient therefrom. Moreover, Since the clathrate compound of the present invention includes a water-soluble microbicide such as CI-MIT as its guest compound, the microbicide therein is stabilized against heat.

The clathrate compound of the present invention may be used, for example, according to the methods mentioned below.

(1) The compound is packed in a column, and a liquid to be treated is passed therethrough.

(2) the compound is put into a bag or a cartridge which is permeable to water but does not dissolve in water, and the bag or cartridge is dipped in or floated above water systems.

(3) The compound of powder or tablet is dispersed in water systems.

(4) The compound is mixed with coating compositions, resins, etc., and the mixture is coated onto the surfaces of a device to be used in water systems, etc.

(5) The compound is adhered to the surfaces of the objects to be protected, by any suitable means.

It is preferred that the clathrate compound of the present invention is added to water to be treated in an amount of from 0.00001 to 0.5 % by weight in terms of the concentration of the water-soluble microbicide such as CI-MIT included in the clathrate compound.

The stability of the clathrate compound of the present invention is often poor in water, when it is added with no other additive. When a nitroalcoholic compound is added to the clathrate compound of the present invention, then the stability of the compound in water may be elevated.

The nitroalcoholic compound to be used for this purpose includes, for example, 2-chloro-2-nitro-ethanol, 1-chloro-1-nitro-2-propanol, 3-chloro-3-nitro-2-butanol, 2-chloro-2-nitro-1,3-butanediol, 1-chloro-1-nitro-2-butanol, 2-chloro-2-nitro-butanol, 2-chloro-2-nitro-3-pentanol, 2,2-dichloro-2-nitro-ethanol, 2-bromo-2-chloro-2-nitro-ethanol, 3-chloro-3-nitro-2,4-pentanediol, 4-chloro-4-nitro-3-hexanol, 2-bromo-2-nitro-ethanol, 2-bromo-2-nitro-3-propanol, 2-bromo-2-nitro-1,3-butanediol, 3-bromo-3-nitro-2,4-pentanediol, 2,2-dibromo-2-nitro-ethanol, 1,1-dibromo-1-nitro-2-propanol, 4-bromo-4-nitro-3-hexanol, 2-fluoro-2-nitro-ethanol, 2-fluoro-2-nitro-1,3-butanediol, 3-iodo-3-nitro-2-butanol, 2-chloro-2-fluoro-2-nitro-ethanol, 2-bromo-2-iodo-2-nitro-ethanol, 2-chloro-2-nitro-1,3-propanediol, 2-bromo-2-nitro-1,3-propanediol. The amount of the compound to be added to the clathrate compound of the present invention is preferably from 0.1 to 5 % by weight relative to the clathrate compound. If it is less than 0.1 % by weight, a sufficient stabilizing effect cannot be attained. However even if it is more than 5 % by weight, no difference in the stability-improving effect will be admitted and such excess addition is not economical.

Where a microbicidal composition comprising the clathrate compound of the present invention and such a nitroalcoholic compound is added to water to be treated therewith, it is preferred that the amount of the composition to be added is approximately from 0.00001 to 0.5 % by weight in terms of the concentration of the water-soluble microbicide in the composition.

The clathrate compound of the present invention is helpful in powdering, stabilizing and concentrating the water-soluble microbicide to be therein. In addition, since the clathrate compound of the present invention is a reaction product having high selectivity in particular compounds, it may also be used for separating and purifying particular water-soluble microbicides. For instance, CI-MIT may be separated from a mixture comprising CI-MIT and its side-product of 2-methyl-4-isothiazolin-3-one (hereinafter referred to as "MI"), though such separation has heretofore been said difficult, by making only CI-MIT selectively included with a host compound to give a clathrate compound, followed by separating the thus-included CI-MIT from the clathrate compound. In this way, a high-purity CI-MIT may be isolated from the mixture. To separate a water-soluble microbicide such as CI-MIT from the clathrate compound including it, the following methods may be employed.

(1) The clathrate compound is dipped in water.

(2) The clathrate compound is dissolved in an organic solvent and then water is added thereto, whereby only the host compound is made precipitated.

According to these methods, the water-soluble microbicide included in the clathrate compound dissolves out into water, and it is recovered as its aqueous solution.

When a water-soluble microbicide is formed into, a clathrate compound with the above-mentioned phenolic compound acting as the host compound, according to the present invention, it becomes solid so that its handleability is much improved. In addition, the dissolution of the microbicide component into water from the clathrate compound is significantly lowered, and the toxicity and the skin-stimulating property of the microbicide are reduced. Moreover, the microbicide in the clathrate compound is prevented from reacting with any other substance to lower its microbicidal activity during its use. Further, the heat-resistant

stability of the microbicide is improved, as being included in the clathrate compound.

For these reasons, the clathrate compound of the present invention may be used effectively as a slow-release microbicide of which the microbicidal activity may be maintained for a long period of time.

In addition, since the clathrate compound of the present invention is helpful in powdering, stabilizing and concentrating the water-soluble microbicide therein and since the host compound selectively includes the water-soluble microbicide therein, the present invention is also useful for separating and purifying water-soluble microbicides.

In particular, when CI-MIT is used as the water-soluble microbicide, the present invention provides an excellent microbicidal preparation

Preferably, the clathrate compound of the present invention is used extremely stably in the form of a microbicidal composition containing the compound along with a predetermined amount of a nitroalcoholic compound.

The present invention will be described in more detail by means of the following examples, which, however, are not intended to restrict the scope of the present invention.

Example 1:

Production of clathrate compound of CI-MIT and 2,4-di-ter-butylphenol (by methanol solvent method):

500 g of a water-soluble microbicide consisting essentially of CI-MIT (CI-MIT concentration: 10.4 % by weight) were extracted with 200 g of chloroform, and the solvent in the chloroform layer was removed by distillation to separate CI-MIT. The yield was 50 g, and the product by weight contained 2 to 3 % by weight of MI.

0.69 g (3.34 mmol) of 2,4-di-ter-butylphenol were put into a sample bottle and dissolved in 10 ml of methanol therein. 0.5 g (3.34 mmol) of the previously separated CI-MIT were added thereto and mixed. After mixing, the mixture was left as it was, thereby removing the solvent therefrom by natural drying to make crystals precipitated. The thus-obtained crystals were separated, washed with 2 ml of water and then dried.

The product was analyzed by IR spectrography and NMR spectrography, and the CI-MIT content in the product was measured by HPLC. As a result, the product was identified to be a clathrate compound of 2,4-di-ter-butylphenol/CI-MIT of being nearly 2/1 (by mol), having a CI-MIT content of 25.83 % by weight.

Example 2:

Production of clathrate compound of CI-MIT and 4,4'-ethylidene-bisphenol (by methanol solvent method):

The same process as in Example 1 was repeated, except that 0.5 g (3.34 mmol) of CI-MIT and the same molar amount of 4,4'-ethylidene-bisphenol were used, and the product was analyzed in the same manner as in Example 1. The product was identified to be a clathrate compound of 4,4'-ethylidene-bisphenol/CI-MIT of being nearly 1/1 (by mol), having a CI-MIT content of 37.84 % by weight.

Example 3:

Production of clathrate compound of CI-MIT and 2,4-di-ter-butylphenol (by water solvent method):

1.436 g (6.95 mmol) of 2,4-di-ter-butylphenol and 10 g of an aqueous microbicidal solution consisting essentially of CI-MIT (CI-MIT concentration: 10.4 % by weight, CI-MIT content: 1.04 g (6.95 mmol)) were mixed and reacted by keeping left them overnight. The crystals thus formed were separated from the aqueous layer, washed with 2 ml of water and then dried.

The product was analyzed by IR spectrography and NMR spectrography, and the CI-MIT content in the product was measured by HPLC. As a result, the product was identified to be a clathrate compound of 2,4-di-ter-butylphenol/CI-MIT of being nearly 2/1, having a CI-MIT content of 25.8 % by weight.

Test Experiment 1:

Test for thermal stability (at 40 °C) of Cl-MIT in its clathrate compound:

5 10 g of each of the clathrate compounds obtained by the methanol solvent method in Examples 1 and 2 were put into a screw-cap bottle, which was then sealed. These bottles were set in a thermostat at 40 °C. At intervals, the content in each bottle was sampled and analyzed by HPLC to determine the Cl-MIT content in the clathrate compound. From the data measured and the initial Cl-MIT content in the fresh compound, the retention percentage of Cl-MIT remained in the sampled clathrate compound was obtained. The results are
10 shown in Table I below.

For comparison, only Cl-MIT was tested in the same manner as above to obtain the retention percentage thereof. The results are also shown in Table 1.

15

20

25

30

35

40

45

50

55

Table 1

No.	Host Compound	Molar Ratio (guest/host)	Retention Percentage of Cl-MIT (%)		
			initial value	after 1 week	after 1 month
1	2,4-Di-tert-butylphenol	1/2	100.0	97.6	97.2
2	4,4'-Ethylidene-bisphenol	1/1	100.0	96.2	96.5
3	(Cl-MIT in the nude)	-	100.0	0.0	0.0

From the test results, it has been confirmed that Cl-MIT in the nude blackened and decomposed in one week while the clathrate compound including Cl-MIT did not.

Test Experiment 2:

Measurement of CI-MIT released into water (at 25 °C) from clathrate compound including it:

5 Each of the clathrate compounds obtained in Examples 1 and 2 was mixed with water to prepare an aqueous mixture having a CI-MIT concentration of 3 % by weight. The thus-prepared mixtures were kept in a thermostat tank at 25 °C and sampled at intervals. Each sample was passed through a 0.45 μ m-millipore filter to thereby separate the clathrate compound from the aqueous phase. Then, the CI-MIT concentration in the thus-separated aqueous phase was measured by HPLC, from which the amount of CI-MIT released
10 into water was determined.

The amount of the clathrate compound tested, the amount of water added to the compound, and the amount of CI-MIT released into water are shown in Table 2.

For comparison, only CI-MIT was tested in the same manner as above to obtain its amount dissolved in water. The results are also shown in Table 2.

Table 2

No.	Host Compound	Amount (g)		Cl-MIT Concentration in Sample (wt.%)	Cl-MIT Concentration in Water (mg/liter) (*1)	Amount of Cl-MIT Released into Water (mg/liter) (*2)			
		Clathrate Compound	Water			after 1 day	after 1 week	after 3 weeks	after 1 month
4	2,4-Di-tert-butylphenol (Cl-MIT content: 25.83 wt.%)	5.784	44.223	3	33940	721 (21.%)	700 (21.%)	681 (2.0%)	664 (2.0%)
5	4,4'-Ethylidene-bisphenol (Cl-MIT content: 37.84 wt.%)	3.137	36.829	3	32554	335 (1.0%)	327 (1.0%)	351 (1.1%)	330 (1.0%)
6	Cl-MIT					30000 (100%)			

(*1) This means the Cl-MIT concentration in water, resulting from complete release of all Cl-MIT from the clathrate compound sample tested.

(*2) The parenthesized value means the percentage of the released Cl-MIT (as the ratio of the released Cl-MIT to the total Cl-MIT in the fresh clathrate compound).

From the test results, it has been confirmed that the release of Cl-MIT into water from the clathrate compound including it was significantly reduced.

Test Example 3:

To the clathrate compound produced in Example 2, containing Cl-MIT included with 4,4'-ethylidene-bisphenol, was added 2-bromo-2-nitro-1,3-propanediol in such an amount as indicated in Table 3 below. The resulting mixture was suspended in water at 60°C in an amount of 1 % by weight in terms of the concentration of Cl-MIT therein. Time-dependent variation in the free Cl-MIT concentration in water and that in the total Cl-MI concentration were measured. The results obtained are shown in Table 3. For comparison, the clathrate compound to which 2,2,2-bromo-2-nitro-1,3-propanediol had not been added was tested in the same manner as above, and the results obtained are also shown in Table 3.

From Table 3, it is obvious that the addition of 2-bromo-2-nitro-1,3-propanediol resulted in the improvement in the stability of the Cl-MIT-including clathrate compound in water.

Table 3

No.	Amount of 2-bromo-2-nitro- 1,3-propanediol (wt.%)	Time	Total Cl-MIT (wt.%)	Free Cl-MIT (ppm)
7	0.05	start	1.09	416
		after 2 weeks	1.10	208
		after 3 weeks	1.08	234
8	0.02	start	1.11	412
		after 2 weeks	1.09	184
		after 3 weeks	1.08	204
9	0.005	start	1.11	388
		after 2 weeks	0	0
		after 3 weeks	0	0
10	0	start	1.11	338
		after 2 weeks	0	0
		after 3 weeks	0	0

As described in detail in the above, the clathrate compound of the present invention has a water-soluble microbicide clathrated by a phenolic compound, and it is helpful in powdering, stabilizing and concentrating the water-soluble microbicide therein. In addition, the present invention is also useful for separating and purifying water-soluble microbicides. Moreover, the present invention, thus providing a water-soluble microbicide as its clathrate compound, has the following advantages:

(1) Since the active ingredient included in the clathrate compound may be slowly released into water from the compound, its microbicidal activity may be maintained for a prolonged period of time.

(2) Since the compound is solid, it may be shaped into tablets, etc. Thus, the handling of the compound is easy.

(3) Since the toxicity and the skin-stimulating property of the microbicide in the compound are lowered, the environment using the microbicide is improved and the safe use of the microbicide is ensured.

(4) The thermal stability of the microbicide in the compound may be elevated, whereby the microbicide is hardly decomposed under heat.

(5) An active ingredient is prevented from reacting with any other substances to lower its microbicidal activity. other substances to lower its microbicidal activity.

Thus, the industrial importance of the present invention is obvious.

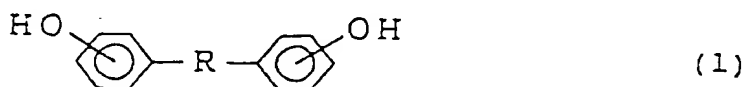
In particular, the present invention preferably uses Cl-MIT as the water-soluble microbicide to be included in the clathrate compound, thus most advantageously displaying the effects.

In addition, the clathrate compound of the present invention may be used extremely stably in the form of a microbicidal composition containing the compound along with a predetermined amount of a nitroalcoholic compound.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A clathrate compound composed of a water-soluble microbicide and a phenolic compound of general formula (1):



wherein R represents an alkylidene group having from 2 to 4 carbon atoms, or of general formula (2):



wherein R¹ and R² each independently represents an alkyl group having from 2 to 4 carbon atoms.

2. A clathrate compound as claimed in claim 1, in which the water-soluble microbicide is 5-chloro-2-methyl-4-isothiazolin-3-one.
3. A clathrate compound as claimed in claim 1 or 2, in which the bisphenolic compound of formula (1) is 4,4'-ethylidenebisphenol, 2,4'-isopropylidenebisphenol, 2,2'-vinylidene bisphenol, 4,4'-isobutylidenebisphenol or 2,6'-sec-butylidene-bisphenol.
4. A clathrate compound as claimed in claim 1 or 2, in which the phenolic compound of formula (2) is 2,4-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,4-di-propylphenol or 2-propyl-4-tert-butylphenol.
5. A clathrate compound as claimed in any one of the preceding claims, in which the molar ratio of the water-soluble microbicide to the bisphenolic compound of formula (1) or (2) is from 1:0.2 to 1:5.
6. A microbicidal composition containing a clathrate compound claimed in any one of the preceding claims and a nitroalcoholic compound.
7. A microbicidal composition as claimed in claim 6, in which the nitroalcoholic compound is 2,2-dibromonitroalcohol.

EP 0 648 415 A2

8. A microbicidal composition as claimed in claim 6 or 7, which contains the nitroalcoholic compound in an amount of from 0.1 to 5% by weight, relative to the clathrate compound.
- 5 9. A method for microbicidal treatment of water, which method comprises adding a clathrate compound claimed in any one of claims 1 to 5 or a microbicidal composition as claimed in any one of claims 6 to 8 to the water to be treated.
- 10 10. A method as claimed in claim 9, in which the clathrate compound or the microbicidal composition is added to water in an amount of from 0.00001 to 0.5% by weight in terms of the concentration of the water-soluble microbicide in said compound.

15

20

25

30

35

40

45

50

55

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



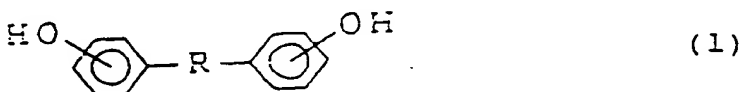
(11) Publication number:

0 648 415 A3

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **94307047.4**(51) Int. Cl.⁶: **A01N 31/08, A01N 43/80,
A01N 25/22, //(A01N31/08,
43:80,25:22)**(22) Date of filing: **27.09.94**(30) Priority: **01.10.93 JP 246888/93**(43) Date of publication of application:
19.04.95 Bulletin 95/16(84) Designated Contracting States:
DE GB NL(88) Date of deferred publication of the search report:
25.10.95 Bulletin 95/43(71) Applicant: **KURITA WATER INDUSTRIES LTD.**
4-7, Nishishinjuku 3-chome
Shinjuku-ku
Tokyo (JP)(72) Inventor: **Yagi, Minoru, Kurita Water Ind.Ltd.****4-7 Nishishinjuku 3-chome**
Shinjuku-ku,
Tokyo (JP)Inventor: **Nakane, Kazumi, Kurita Water**
Ind.Ltd.**4-7 Nishishinjuku 3-chome**
Shinjuku-ku,
Tokyo (JP)Inventor: **Hiyane, Yuriko, Kurita Water Ind.Ltd.****4-7 Nishishinjuku 3-chome**
Shinjuku-ku,
Tokyo (JP)(74) Representative: **Pendlebury, Anthony et al**
PAGE, WHITE & FARRER
54 Doughty Street
London WC1N 2LS (GB)(54) **Clathrate compound including water-soluble microbicide.**

(57) 1. A clathrate compound composed of a water-soluble microbicide and a phenolic compound of general formula (1):



wherein R represents an alkylidene group having from 2 to 4 carbon atoms,
or of general formula (2):



wherein R¹ and R² each independently represents an alkyl group having from 2 to 4 carbon atoms.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 7047

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	US-A-5 082 654 (SUGI H ET AL) 21 January 1992 see col. 2, l. 17-44; col. 3, l. 37 - 68. ---	1-10	A01N31/08 A01N43/80 A01N25/22 //(A01N31/08, 43:80,25:22)
Y	DATABASE WPI Section Ch, Week 9203 Derwent Publications Ltd., London, GB; Class D22, AN 92-021493 & JP-A-03 271 204 (KURITA WATER IND KK) , 3 December 1991 * abstract *	1-10	
Y	DATABASE WPI Section Ch, Week 9204 Derwent Publications Ltd., London, GB; Class C02, AN 92-030653 & JP-A-03 279 373 (KURITA WATER IND KK) , 10 December 1991 * abstract *	1-10	
Y	EP-A-0 327 214 (KURITA WATER IND KK) 9 August 1989 * the whole document *	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Y,D	EP-A-0 326 262 (KURITA WATER IND LTD) 2 August 1989 * the whole document *	1-10	A01N
Y	EP-A-0 326 261 (KURITA WATER IND LTD) 2 August 1989 * the whole document *	1-10	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 8 August 1995	Examiner Klaver, J
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 (01.82) (P04/001)